Calibration Report: Winkler titrations for total dissolved O_2 concentration and saturation

Instrument name: WHOI BOOMLAB Winkler autotitrator

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Brief description of protocol and relation to biogeochemical stocks: The O_2 concentration and saturation in seawater reflect a multitude of biological and physical processes, including photosynthesis, respiration, bubble injection through breaking waves, mixing of water masses, temperature and atmospheric pressure changes. The method for determining O_2 concentration in seawater was originally presented by Winkler (1888). We use the modified version of Carpenter (1965) as outlined in the WOCE Standard Operating Procedures Manual (Dickson, 1996). Briefly, O_2 in a known volume of sample oxidizes iodide ions (I^-) to iodine (I_2). The amount of iodine generated through this reaction is quantitatively titrated with a standard of thiosulfate ($S_2O_3^{-2}$) using an automated potentiometric end-point titrator. The conversion stoichiometry is four moles of thiosulfate for every mole of O_2. This assay is appropriate for measuring O_2 concentration in seawater under most oceanic conditions when hydrogen sulfide is not present. These data will be used to measure O_2 concentration and saturation and most importantly to calibrate the O_2 sensors (optodes).

Other contributing protocols: This is complementary to the Equilibrator Inlet Mass Spectrometer measurements which specifically measures the biological O_2 saturation and concentration. From these two methods, the physical O_2 supersaturation can be derived.

Uncertainties and quality control concerns: Samples for O_2 analyses will be collected at multiple stations. The main purpose is to calibrate and validate the O_2 sensors data on the ships and the autonomous platforms. Samples will be collected in triplicates to check replication error and precision. Precision and accuracy of dissolved O_2 concentration measurements should be 0.2% of air saturation or better (coefficient of variation). Air saturation values are calculated relative to the salinity and temperature dependent solubility of oxygen in seawater (Garcia and Gordon, 1992).

Data products originating with this method:

Parameter	Units
Dissolved O_2 concentration	$\mu mol\ kg^{-1}$
Total O_2 saturation	%

During the 2018 EXPORTS North Pacific cruise, Winkler titrations were conducted on the R/V Sally Ride by Weiyi Tang, Duke University with assistance from Alex Niebergall, Duke University using reagents and equipment provided by the Nicholson Lab at WHOI. The WHOI titrator is a custom designed autotitrator with automated potentiometric endpoint detection. Over the course of the cruise, 287 individual Winkler bottle samples from calibration casts were titrated. Titrations on five calibration casts were conducted for the Seaglider, four for the Lagrangian Float, three for the BGC Argo float and one for the Wirewalker. Most were sampled as sets of triplicates with each replicate drawn from a different Niskin bottle fired at the same depth. Of the 287 samples, 3 were flagged as unexplained outliers and 6 were flagged due to identified problems that included Niskin misfires, a broken flask, and a software crash. Subsequent results are reported for the remaining 278 samples. Oxygen concentration ranged from 16.5 µmol kg^{-1} to 300.9 µmol kg^{-1}. The median standard deviation for triplicate samples was 0.52 µmol kg^{-1} (0.2% of saturation).

Oxygen concentration were determined in units of µmol kg^{-1} follow the WOCE protocol (Dickson 1996). A brief overview is outlined here. Molarity of thiosulfate used in titrations was determined from repeated titrations of 10 mL aliquots from a calibrated dispensette of a 0.1 N potassium iodate standard solution such that:

$$M_{thios} = \frac{6(V_{KIO_3} M_{KIO_3})}{V_{end} - V_{blank}} \qquad (1)$$

A total of 28 standard titrations were conducted through the cruise and values of M_{thios} = 0.190246 ± 1.2810×10^{-4} M and $V_{blank} = 2.77\times10^{-6} \pm 0.33\times10^{-6}$ L.

$$n_{O_2} = \frac{M_{thios}(V_{end} - V_{blank})}{4} - 7.6\times10^{-8} \qquad (2)$$

Where n_{O_2} is the number of moles of sample oxygen titrated and 7.6×10^{-8} is a correction factor for the oxygen content of reagents added to the titration.
Oxygen sample concentration ($C(O_2)$) then was calculated based on the pre-calibrated volume of each titration flask (V_{flask}):

$$C(O_2) = 10^9 \frac{n_{O_2}}{(V_{flask} - 2\times10^{-3})\rho_{sw}(S,T)} \qquad (3)$$

where -2×10^{-3} is the volume displaced by 2 mL of added reagent, $\rho_{sw}(S,T)$ is seawater density in kg m^{-3} and 10^9 converts to standard units of µmol kg^{-1}.

Subsequently concentration units were converted to ml L^{-1} as required by SeaBASS using the equation:

$$O_2(ml/L) = O_2(\mu mol/kg) * 22.392 * (\sigma_\theta + 1000) * 10^{-6} \qquad (4)$$

where 22.392 is the virial molar volume of oxygen (L mol^{-1}) and σ_θ is potential density.

The equilibrium dissolved oxygen concentration (O_2eq) was calculated using the TEOS Gibbs Seawater Toolbox function gsw_O2sol_SP_pt.m which returns units of μmol kg^{-1}. Dissolved oxygen saturation is then calculated as:

$$O_2 \text{ saturation} = 100 * O_2(\mu mol/kg) / O_2eq \tag{5}$$

Key method references:

1. Winkler, L.W. (1888). Die Bestimmung des in Wasser gelösten Sauerstoffen. Berichte der Deutschen Chemischen Gesellschaft, 21: 2843–2855.
2. Carpenter, J.H. (1965). The Chesapeake Bay Institute Technique for the Winkler Dissolved Oxygen Method. *Limnology and Oceanography*, *10*(1), 141–143. https://doi.org/10.4319/lo.1965.10.1.0141
3. Strickland, J.D.H., and Parsons, T.R. (1968). Determination of dissolved oxygen. in A Practical Handbook of Seawater Analysis. Fisheries Research Board of Canada, Bulletin, 167, 71–75.
4. Dickson, A (1996) Determination of dissolved oxygen in sea water by Winkler titration, Accessed at: https://www.nodc.noaa.gov/woce/woce_v3/wocedata_1/whp/manuals/pdf/91_1/dickson2.pdf
5. Garcia, H. E., & Gordon, L. I. (1992). Oxygen solubility in seawater: Better fitting equations. *Limnology and Oceanography*, *37*(6), 1307–1312. https://doi.org/10.4319/lo.1992.37.6.1307